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# Experimentelle Untersuchung des Verbunds zwischen Polyetheretherketon (PEEK) und unterschiedlichen Verblendmaterialien

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## Abkürzungsverzeichnis

|         |                                                   |
|---------|---------------------------------------------------|
| ANOVA   | Analysis of variance                              |
| Bis-GMA | Bisphenol-A-(di)-methacrylat                      |
| CAD     | Computer aided design                             |
| CAM     | Computer aided manufacturing                      |
| CI      | Confidence intervall                              |
| DB      | dialog bonding fluid                              |
| DM      | Dimethacrylat                                     |
| FDP     | Fixed dental prosthesis                           |
| HEMA    | Hydroxy-ethyl-methacrylat                         |
| MDP     | 10-Methacryloyloxydecylhydrogenphosphat           |
| MH      | Monobond Plus / Heliobond                         |
| MMA     | Methylmethacrylat                                 |
| PAEK    | Polyaryletherketon                                |
| PEEK    | Polyetheretherketon                               |
| PEKEKK  | Polyetherketonetherketonketon                     |
| PEKK    | Polyetherketonketon                               |
| PETIA   | Pentaerythritol triacrylate                       |
| SD      | Standard deviation                                |
| SIC     | Silicone carbide papers                           |
| STL     | StereoLithography, Standard Tessellation Language |
| SU      | Scotchbond Universal                              |
| TBS     | Tensile bond strength                             |
| TEGDMA  | Triethylen-glycol-dimethacrylat                   |
| UDMA    | Urethandimethacrylat                              |
| VL      | visio.link                                        |

## Publikationsliste

1. **Taufall S**, Eichberger M, Schmidlin PR, Stawarczyk B. Fracture load and failure types of different veneered polyetheretherketone fixed dental prostheses. Clin Oral Investig 2016;20(9):2493-2500 (Impact factor 2016: 2,308)
2. Stawarczyk B, **Taufall S**, Roos M, Schmidlin PR, Lümke mann M. Bonding of composite resins to PEEK: the influence of adhesive systems and air-abrasion parameters. Clin Oral Investig 2018;22(2):763-771 (Impact factor 2016: 2,308)

## Eidesstattliche Versicherung

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Ich erkläre hiermit an Eides statt,

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**Experimentelle Untersuchung des Verbunds zwischen Polyetheretherketon (PEEK)  
und unterschiedlichen Verblendmaterialien**

selbständig verfasst, mich außer der angegebenen keiner weiteren Hilfsmittel bedient und alle Erkenntnisse, die aus dem Schrifttum ganz oder annähernd übernommen sind, als solche kenntlich gemacht und nach ihrer Herkunft unter Bezeichnung der Fundstelle einzeln nachgewiesen habe.

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München, den 16.04.2018

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Ort, Datum

**Simon David Taufall**

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Unterschrift Doktorandin/Doktorand

Meinen Eltern, meinem Bruder Jan und meinen Großeltern  
für Ihre bedingungslose finanzielle und moralische Unterstützung und  
das immer offene Ohr  
sowie  
der Liebe meines Lebens Lena  
dafür, dass Sie mich unendlich geduldig erträgt und mir Mut macht  
wenn ich zweifle

## **1 Einleitung und wissenschaftliche Zielsetzung**

Der technische Fortschritt der Industrienationen hat in den letzten Jahrzehnten unter anderem das medizinische Gebiet stark beeinflusst. Die Vervielfachung der Kosten für medizinische Versorgung durch immer aufwendigere und teurer werdende Technologien führte zu Einschränkungen der Leistungen der gesetzlichen ebenso wie der privaten Krankenkassen, wovon auch der zahnmedizinische Bereich betroffen war und ist. Daraus resultiert eine wachsende Anzahl an Patienten, die sich aus wirtschaftlichen Gründen eine prothetische Versorgung nicht zum Zeitpunkt der Notwendigkeit oder aber auch überhaupt nicht anfertigen lassen können.

Darüber hinaus zeigt sich eine generelle Zunahme des Anteils der Bevölkerung der unter Allergien leidet, wobei Nickel in diesem Kontext unter den Nichtedelmetallwerkstoffen in der Zahnmedizin die größte Rolle spielt.

Die Suche nach günstigeren sowie verträglicheren Alternativen führte über Keramiken, die aufgrund ihrer großen Härte bei natürlichen Antagonisten stärkere Abrasionen verursachen im Vergleich zu Kunststoffen, die in der Industrie bereits Anwendung finden und eine hohe Stabilität aufweisen. Hierbei wurden die Polyaryletherketone (PAEK), die aufgrund ihrer hohen massenbezogenen Stabilität z.B. schon in der Luftfahrt eingesetzt werden, als vielversprechend betrachtet.

Nach und nach hielten vor allem Polyetheretherketone (PEEK) und Polyaryletherketonketone (PEKK) Einzug in den medizinischen Bereich. Neben der gezeigten Biokompatibilität zeichnen sich diese Materialien durch hohe thermische, chemische und radiologische Stabilität sowie die Möglichkeit der maschinellen Bearbeitung in CAD/CAM-Systemen aus.

In den durchgeführten Untersuchungen, die im Folgenden gezeigt werden, wurde im speziellen der Werkstoff PEEK untersucht, der in der Humanmedizin bereits als Knochenersatz z.B. im Bereich von Wirbelkörpern Einsatz findet.

Das Material wird im Allgemeinen in CAM-Fräsmaschinen aus dem Vollmaterial subtraktiv geformt oder aus Granulat oder Pellets gepresst. Neu ist die Verarbeitung im dreidimensionalen Druck mittels PEEK-Filamenten. Optisch hat PEEK eine weißlich-graue Färbung bei vollständiger Opazität, was beim Einsatz als festsitzenden dauerhaften Zahnersatz im Sichtbereich eine Verblendung notwendig macht. Hierbei scheiden Keramiken aufgrund der notwendigen hohen Brenntemperatur aus, weshalb die Nutzung von Kunststoffen als Verblendung sowohl aufgrund der gleichen Werkstoffgruppe und damit auch ähnlichen Werkstoffeigenschaften als auch der jahrelangen Erfahrungen mit diesen Materialien in der Prothetik am nächsten liegt.

Die Breite an verfügbaren Kunststoffen sowie die unterschiedlichen technischen Verfahren zur Herstellung von ebensolchen Verblendungen machen in-vitro Untersuchungen zur Stabilität der Restaurationen vor Untersuchungen an Patienten notwendig.

Darüber hinaus müssen die Verblendungen jeglicher Art mit dem Gerüst aus PEEK gefügt werden. Die Fügetechnik bzw. die Materialien, die bei der Fügung Verwendung finden, stellen den Haupteinfluss auf die Stabilität des Verbundes und damit auf die Stabilität der gesamten Restauration dar, weshalb auf diesem Gebiet weitere Untersuchungen durchgeführt werden sollten. Maßgeblichen Einfluss auf den Verbund hat zum einen die Oberflächenbehandlung, zum anderen spielt der eingesetzte chemische Haftvermittler eine übergeordnete Rolle.

Die beiden Untersuchungen, die im Rahmen dieser Arbeit durchgeführt wurden, haben diese beiden Fragestellungen behandelt.

In der ersten Untersuchung wurden standardisierte dreigliedrige Brücken mit zwei Brückenpfeilern von einem Eckzahn auf einen Prämolaren mit Ersatz eines Prämolaren durch ein Brückenglied mit unterschiedlichen Verblendungen hergestellt und auf ihre Stabilität getestet. Hierbei waren die Verblendungen zum einen von der Materialseite als auch von der Art der Herstellung unterschiedlich.



In der zweiten Arbeit wurde eine Auffälligkeit aus einer vorangegangenen und der o.g. Arbeit zum Anlass genommen unterschiedliche Vorbehandlungen der PEEK-Oberfläche mit unterschiedlichen chemischen Haftvermittlern zu paaren und die Festigkeit des Verbunds zu untersuchen.

## 2 Eigene Arbeit

Im Folgenden werden zwei in englischer Sprache verfasste Originalarbeiten vorgestellt und diskutiert.

### 2.1 Originalarbeit: **Taufall S, Eichberger M, Schmidlin PR, Stawarczyk B.** **Fracture load and failure types of different veneered polyetheretherketone fixed dental prostheses. Clin Oral Investig 2016;20(9):2493-2500. (Impact factor 2016: 2,308)**

#### ***Zusammenfassung:***

Ziel: Ziel dieser Untersuchung war, die Bruchlast von verschiedenen verblendetem, 3-gliedrigem, festsitzenden Zahnersatz aus PEEK nach unterschiedlicher Alterung zu untersuchen und zu vergleichen.

Material und Methode: Anatomisch kongruent geformte, 3-gliedrige Brücken wurden unter Verwendung eines Master-STL-Datensatz aus PEEK-Ronden gefräst und zufällig in vier Gruppen eingeteilt (n = 120, n = 30 pro Verblendungsart), die unterschiedlich verblendet wurden: (i) digitale Verblendung mit breCAM.HIPC, (ii) herkömmliche Verblendung mit crea.lign, (iii) herkömmliche Verblendung mit crea.lign Paste, und (iv) Verblendung unter Verwendung von vorgefertigten Verblendungen mit visio.lign. Die Brücken wurden nach Fertigstellung auf einen Abutment aus CoCrMo-Legierung befestigt und anschließend in einer Universal-Prüfmaschine (1 mm / min) die Bruchlast ermittelt. Die Prüfung wurde mit der zufällig ausgewählten Hälfte jeder Gruppe vor und nach einem Alterungsverfahren (10000 Thermozyklen, 5/55 °C) durchgeführt. Für die statistische Datenanalyse (p < 0,05) wurde Zwei- und Ein-Weg ANOVA, gefolgt von Post-hoc-Tests (Scheffé) verwendet.

Ergebnisse: Die Untersuchung hat gezeigt, dass die Methode bzw. das Material der Verblendung unabhängig von der Alterungsstufe Einfluss auf die Bruchlastergebnisse hat. Die höchste Bruchbelastung wurde für die Brücken mit digitaler Verblendung ( $1882 \pm 152$  N initial,

2021  $\pm$  184 N nach Thermozyklierung) gemessen. Die übrigen Gruppen zeigten vergleichbare Ergebnisse, wobei keine Auswirkungen der thermischen Alterung beobachtet wurden. Digitale und konventionelle Verblendungen zeigten als Versagensart nach den Bruchtests Risse in der Region des Brückenglieds, welche vom Bereich des Verbinders ausgingen, während die vorgefertigten Verblendungen überwiegend ein Versagen des adhäsiven Verbundes zeigten.

Schlussfolgerung: Bei der digitalen Verblendung konnten die höchsten Bruchlastwerte gemessen werden. Die thermische Alterung zeigte unabhängig von der Verblendung keine Auswirkung auf die Bruchlast aller getesteten 3-gliedrigen Brücken aus PEEK.

Klinische Relevanz: Laut der Ergebnisse dieser Studie kann die zuverlässigste Verblendung von PEEK-Gerüsten mittels der digitalen Verblendung erreicht werden.



## Fracture load and failure types of different veneered polyetheretherketone fixed dental prostheses

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### Abstract

**Objective** The aim of this study is to investigate the fracture load of different veneered PEEK 3-unit fixed dental prosthesis (FDPs) after different aging regimens.

**Methods** Congruently anatomically shaped 3-unit FDPs were milled using a master stl-data set and randomly divided into four groups ( $N=120$ ,  $n=30$  per veneering group), which were veneered using different veneering methods: (i) digital veneering with breCAM.HIPC, (ii) conventional veneering with crea.lign, (iii) conventional with crea.lign paste, and (iv) using pre-manufactured veneers visio.lign. The FDPs were then adhesively cemented on a metal abutment and fracture loads were measured in a universal testing machine (1 mm/min) before and after aging (10,000 thermal cycles, 5/55 °C). Two- and one-way ANOVA followed by post hoc Scheffé tests were used for data analysis ( $p<0.05$ ).

**Results** This investigation showed an influence of the veneering method on the fracture load results independent of the aging level. The highest fracture load was measured for the FDPs with digital veneering ( $1882 \pm 152$  N at baseline,  $2021 \pm 184$  N after thermocycling). The remaining groups showed comparable results, and no impact of thermal aging was observed. Digital and conventional veneers showed cracks in the pontic region starting from the connector area as a main failure

type after loading, while the pre-manufactured veneers showed predominantly adhesive failures.

**Conclusions** The digital veneering method showed the highest fracture load resistance. Thermal aging showed no impact on the fracture load of all tested veneered PEEK 3-unit FDPs.

**Clinical relevance** According to this study results, reliable veneering of PEEK FDPs can be achieved with digital veneering.

**Keywords** Fracture load · PEEK · Digital veneering · Veneering resin composite

### Introduction

The search for biocompatible bone replacement materials in medicine with mechanical characteristics comparable to human bone as an alternative to metals led to plastics, which are used in industrial applications and have a high stability. Polyaryletherketones (PAEK), due to their high mass-based stability and resistance against temperatures, stress, and corrosion, were the first promising candidates [1]. Mainly polyaryletheretherketone (PEEK), polyetherketoneketone (PEKK), and polyaryletherketoneetherketoneketone (PEKEKK) found their way into the medical field [2]. In addition to their high biocompatibility, these materials are characterized by high thermal, chemical, and radiological stability. PEEK is a high-temperature polymer selected from the family of the aforementioned PAEK with outstanding mechanical characteristics [3, 4]. It consists of an aromatic basic structure interconnected by ketones and ether functional groups, which can be classified as a semi-crystalline thermoplastic [5]. Because of the abovementioned characteristics, in particular the good milling and grinding properties combined with high

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stability [6] similar to the stability of human bone [3], it is already used in various medical applications such as spine implant or bone substitute technology for large bone defects in traumatology [7, 8].

PEEK is also being used in dentistry as abutment, removable partial denture frameworks, and fixed dental prosthetic framework (FDP, fixed dental prosthesis) [9]. In general, there are two production methods for PEEK FDPs which are press technology or computer aided design/computer aided manufacturing (CAD/CAM). The latter shows lower deformations pattern and higher fracture load values [10, 11].

PEEK is opaque and has generally a white to gray color; however, first tooth-colored materials were already introduced to the market. As it is not esthetic, the material cannot be used for monolithic prosthetic solutions in the visible area, making an additional veneering indispensable. The fracture load of a 3-unit PEEK framework without veneering was reported to be 1385 N, which corresponds to be about 2.5 times the average bite force [12] in the posterior area [5].

A variety of studies of bond strength between veneering resin composite and PEEK framework have been performed already, in which different pre-treatments of the airborne-particle abraded surface with piranha-etching [13–16], sulfuric acid [5, 9, 12, 17], and cold plasma treatment [18, 19] were tested, providing, however, some conflicting results. Some of these studies examined the influence of the adhesive on the bond strength to PEEK and the vast majority showed nevertheless adequate bonding results with MMA-based adhesive materials comparable to those of conventional framework materials like ceramic or metal alloys [14–16, 20–22].

A first peer-reviewed study of veneered PEEK FDPs showed no impact of PEEK surface pre-treatment and veneering material on the fracture load results [23]. After thermal cycling, however, all veneered FDPs still showed cracks in the veneering material in the pontic region. After loading, no fractures of the PEEK frameworks were evident in any FDPs, but chipping directly between PEEK and veneering resin composite was observed. This study used two differently filled (86 versus 74 % w/w) veneering composite resins based on the same matrix. The FDPs, which were veneered using the lower filled veneering composite material tended to result in higher fracture loads than those veneered with the higher filled material [23]. In that study—in relation to physiologic mastication forces of 400 N—values up to 277 N for the veneered FDPs were observed. In contrast, PEEK FDPs without veneering showed much higher fracture load results (2354 N) [10]. Because esthetic concerns remain an important clinical reality and benchmark, veneered FDPs should always be assessed, especially because they contrast with standard tests with simplified geometric specimens. Using this approach, however, the fracture load represents the internal tensile stresses within the FDPs after veneering and thermal stress, as well as the bond and flexural strength of the framework together with

the veneering resin composite, which results in the lower fracture load of the previous study. Therefore, the authors stated that further in vitro and in vivo studies and optimization of the veneering process are still warranted. Therefore, this study investigated different veneering methods for PEEK frameworks on the fracture load results. The null hypothesis of this study was to test that the veneering method had no influence on the fracture load of PEEK FDPs with four different veneering methods, i.e., one digital, two conventional, and one pre-manufactured veneer technique.

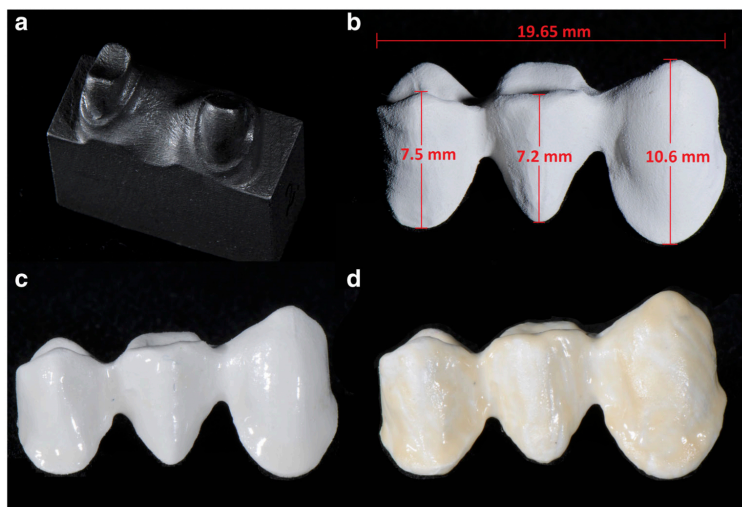
## Materials and methods

The 3-unit Co-Cr-Mo master abutment model ranging from a canine to a second premolar (Fig. 1a) and the PEEK framework used in this study are described in more detail elsewhere [23]. The resulting pontics (Fig. 1b) of the PEEK framework had a 1-mm circular edge, a concave base, and a sharp chamfer. Each connector amounted for an area of 11.3 mm<sup>2</sup>, a width of 3.8 mm, and a height of 3.2 mm. The thickness of the framework was set at 0.6 mm.

Based on this design, a total of 120 congruent frameworks were milled (Zeno Tec 4030 M1; Wieland Dental + Technik, Pforzheim, Germany) from PEEK blanks (breCAM.BioHPP Discs, bredent, Senden, Germany, Lot: 400177). After detaching the frameworks and removing the mill connectors, the FDPs were abraded with airborne-particles with 110 µm Al<sub>2</sub>O<sub>3</sub> powder at 0.25 MPa, at an angle of 45° from a distance of 10 mm (basic Quattro IS; Renfert, Hilzingen, Germany), and subsequently put in an ultrasonic bath for 5 min (L&R Transistor Ultrasonic T14, L&R, Kearny, NY, USA), which was filled with deionized water. Afterwards, the frameworks were conditioned using visio.link (bredent, Lot: 141432; composition: MMA, products of reaction of 2-propenoic acid with pentaerythritol; diphenyl-(2,4,6-trimethylbenzoyl)-phosphineoxide). Because visio.link is a MMA-based adhesive system and most of the recent publications demonstrated that an adequate chemical bond to PEEK can be established [14–16, 20, 21, 24] with this material, conditioning was carried out by wetting the frameworks with a thin film using a microbrush which was immediately polymerized for 90 s (intensity: 220 mW/cm<sup>2</sup>, Brelux Power Unit; bredent) (Fig. 1c), before a thin film of opaquer (Opaquer combo.lign; bredent) was applied and polymerized for 360 s (Fig. 1d).

The specimens were randomly divided into four veneering groups (*n*=30/group) as described in Table 1: (i) digital veneering with breCAM.HIPC (bredent; Lot No. 406700), (ii) conventional veneering with veneering composite resin crea.lign (bredent; Lot No. 130513), (iii) conventional veneering with veneering composite resin crea.lign paste (bredent; Lot No. 134524, 141207), and (iv) veneering using bonding

**Fig. 1** **a** The master 3-unit from canine to second premolar Co-Cr-Mo abutment model (*up, left*). **b** PEEK pontic framework (*up, right*). **c** visio.link conditioned PEEK framework (*down, left*). **d** Conditioned PEEK framework with polymerized opaquer combo.lign (*down, right*)



of pre-manufactured veneers visio.lign (bredent; Lot No. Z3304499, Z3843532, Z3849293, Z3303681).

For the first group with the digital veneering, a master FDP with the visio.lign veneers and waxing was manufactured. The shape of the pre-manufactured veneers was taken into account, which can only slightly be changed. In the middle of the pontic region of the first premolar, an impression was formed centrally using a ball ( $d=6$  mm) creating a 3-point contact for the load type during the fracture load test. The design described before results in a thickness of the veneering between 0.8 and 1.2 mm as visualized in the crosscut of a connector in Fig. 2. Then two scans (3 Shape; strip light scanner; Wieland Dental + Technik) were performed, one from the PEEK framework on the metal abutment model and another one from the master FDP on the metal abutment model (Fig. 3). These scans were subtracted from each other and led to the design of the digital veneer which

was subsequently milled (Zeno Tec 4030 M1; Wieland Dental) from breCAM.BioHPP discs. After detaching of the veneers and removing the mill connectors, the veneers were airborne-particle abraded from inside with  $110\text{ }\mu\text{m}$   $\text{Al}_2\text{O}_3$  powder at 0.25 MPa at an angle of  $45^\circ$  from a distance of 10 mm, and subsequently put in an ultrasonic bath filled with deionized water for 5 min. Immediately after drying the inner surface, the veneers were conditioned from inside with visio.link (bredent, Lot: 141432) and polymerized for 90 s. The prepared frameworks were put on the alloy models and the veneers were filled with combo.lign (bredent; Lot No. 132420) before pressing them on the frameworks and polymerizing them for 180 s at  $220\text{ mW/cm}^2$  (brelux Power Unit; bredent). After removing the surplus, the FDPs were polished (Opal L, Renfert; Lot No. 520-0001; Abraso Starglanz; bredent) by a blinded operator (S.T.) (Fig. 3).

**Table 1** Study design

|           |                                                         |                            |                                 |                            |                                                    |                            |                                                                                                         |                            |
|-----------|---------------------------------------------------------|----------------------------|---------------------------------|----------------------------|----------------------------------------------------|----------------------------|---------------------------------------------------------------------------------------------------------|----------------------------|
| Framework | breCAM.BioHPP (PEEK) N=120 LOT: 400177                  |                            |                                 |                            |                                                    |                            |                                                                                                         |                            |
| Veneer    | Digital veneers<br>breCAM.HIPC<br>(n=30)<br>LOT: 406700 |                            | Conventionell veneers           |                            |                                                    |                            | Premanufactured<br>veneers<br>visio.lign<br>(n=30)<br>LOT: Z3304499<br>Z3843532<br>Z3849293<br>Z3303681 |                            |
|           |                                                         |                            | crea.lign (n=30)<br>LOT: 130513 |                            | crea.lign paste<br>(n=30)<br>LOT: 134524<br>141207 |                            |                                                                                                         |                            |
| Aging     | initial                                                 | 10000<br>thermo-<br>cycles | initial                         | 10000<br>thermo-<br>cycles | initial                                            | 10000<br>thermo-<br>cycles | initial                                                                                                 | 10000<br>thermo-<br>cycles |
| Quantity  | 15                                                      | 15                         | 15                              | 15                         | 15                                                 | 15                         | 15                                                                                                      | 15                         |





**Fig. 2** Crosscut of a HIPC veneered FDP in the connector area

The second and third group used a conventional veneering composite resin material. For the second group, a translucent silicone moulding (visio.sil; bredent) of the master bridge was manufactured, but because of the third group's resin exhibited a higher viscosity, a two-piece moulding was used for the latter group, which was also made of a translucent light polymerizing plastic material (Versyo.putty; Heraeus Kulzer, Hanau, Germany). The PEEK frameworks for the two groups were additionally prepared with a second opaque liner (crea.lign opaquer; bredent; Lot No. 131137) and polymerized for 360 s (brelux Power Unit). Afterwards, the moulding was filled with the composite resin (crea.lign for the second group and crea.lign paste for the third group) and the alloy model with the attached PEEK framework was pressed into the silicon moulding. Refinement and polishing were carried out as described above.

The fourth group was veneered using pre-manufactured veneers (visio.lign) which covered only the vestibular side. The veneers were ground using a mould of silicon (visio.sil) of the master FDP to fit the shape. Refining was carried out as mentioned before, using a masked operator (S.T.) focusing on the shape, which should fit the master FDP again. Polishing was carried out as described above.

The FDPs were then randomly allocated to two groups per veneering material and aging level. One half of each veneering group was thermocycled (Thermocycler THE 1100; SD Mechatronik, Feldkirchen-Westerham, Germany) from 5 to 55 °C with a dwell time of 20 s for 10,000 cycles. Thereafter, all FDPs were adhesively fixed on the airborne-particle abraded and visio.link conditioned CoCrMo alloy models using Multilink Automix (Ivoclar Vivadent, Schaan, Liechtenstein; Lot No. 503821) and a standardized load of

100 N for 15 min. Then the specimens were stored for 48 h in deionized water at 37 °C. Load-bearing tests were carried out using a standardized machine (Zwick 1445; Zwick, Ulm, Germany). For that the FDPs were positioned in the machine, a tin foil of 0.5 mm thickness was positioned on the FDP and the stress stamp to avoid force peaks. Subsequently the stress stamp of hemispherical shape ( $D=6$  mm) was positioned in the mould in the occlusal area of the first premolar. The load was applied from the vertical direction at a crosshead speed of 1 mm per minute (Fig. 4). Failure was defined as the moment at which the measured force of the load dropped by 10 % under the maximum point.

The Kolmogorov-Smirnov test was used to verify a normality of data distribution. Descriptive statistics (mean, standard deviation (SD), 95 % confidence intervals (CI)) were computed. Significant differences between the groups were tested with two-way and one-way ANOVA, followed by the Scheffé post hoc test. All statistical tests were calculated using IBM SPSS (Version 23; IBM Corporation, Armonk, New York, USA) ( $p<0.05$ ).

## Results

The descriptive statistics are summarized in Table 2. The Kolmogorov-Smirnov test indicated no evidence for violation of normality assumption regarding the distribution of the data ( $p<0.05$ ). According to the two-way ANOVA, the results showed that the veneering method ( $p<0.001$ ) had a significant effect on the fracture load results of the tested PEEK FDPs. In contrast, the aging level ( $p=0.798$ ) as well as the interaction between both parameters were not significant ( $p=0.290$ ). Subsequently, the data set was split based on aging level and the impact factor of the veneering methods was analyzed separately.

Digitally veneered FDPs showed significantly higher fracture load results compared to the remaining veneering groups ( $p<0.001$ ), regardless of the aging level. The remaining groups were in the same value range.

The fracture type analysis showed two typical modes. For the first three groups, i.e., the digital and conventional veneering, results showed that the fracture type was comparable and showed cracks in the veneering in the pontic



**Fig. 3** PEEK framework on the metal abutment model (powder conditioned for 3D-Scan); Master FDP on the metal abutment model

(powder conditioned for 3D-Scan); FDP with PEEK framework and digital veneer (from left to right)



**Fig. 4** FDP positioned in the testing machine with tin foil and stress stamp of hemispherical shape



**Fig. 5** Example for fracture type of the first three groups, showing cracks in the pontic region starting from the connector

region starting from the connector area (Fig. 5). In the fourth group, the failure type of the pre-manufactured veneering could not be visually detected. However, the load-bearing curves showed a failure and also acoustically a distinct crack could be heard. Hence, an adhesive failure between the PEEK-framework and pre-manufactured

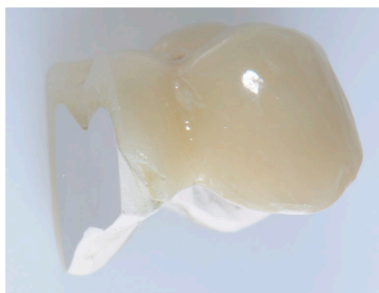
veneering was assumed. After cutting of the tested FDPs, a final failure can be excluded. The failure was caused by an adhesive breakdown between the visio.link layer and the PEEK framework in all cases, as evidenced by the completely exposed PEEK surface (Fig. 6).

**Table 2** Statistic results

|                    |                                                         |                                |                                    |                                        |                                                   |                                |                                                                                                         |                            |
|--------------------|---------------------------------------------------------|--------------------------------|------------------------------------|----------------------------------------|---------------------------------------------------|--------------------------------|---------------------------------------------------------------------------------------------------------|----------------------------|
| Framework          | breCAM.BioHPP (PEEK) N=120 LOT: 400177                  |                                |                                    |                                        |                                                   |                                |                                                                                                         |                            |
| Veneer             | Digital veneers<br>breCAM.HIPC<br>(n=30)<br>LOT: 406700 |                                | Conventionell veneers              |                                        |                                                   |                                | Premanufactured<br>veneers<br>visio.lign<br>(n=30)<br>LOT: Z3304499<br>Z3843532<br>Z3849293<br>Z3303681 |                            |
|                    |                                                         |                                | crea.lign<br>(n=30)<br>LOT: 130513 |                                        | crea.lign paste<br>(n=30)<br>LOT:134524<br>141207 |                                |                                                                                                         |                            |
| Aging              | initial                                                 | 10000<br>therm<br>o-<br>cycles | initial                            | 1000<br>0<br>therm<br>o-<br>cycle<br>s | initial                                           | 10000<br>therm<br>o-<br>cycles | initial                                                                                                 | 10000<br>thermo<br>-cycles |
| Mean [N]           | 1882 <sup>b</sup>                                       | 2021 <sup>b</sup>              | 1138 <sup>a</sup>                  | 1008 <sup>a</sup>                      | 1226 <sup>a</sup>                                 | 1229 <sup>a</sup>              | 1213 <sup>a</sup>                                                                                       | 1149 <sup>a</sup>          |
| Mean-deviation [n] | 152                                                     | 184                            | 278                                | 372                                    | 280                                               | 239                            | 380                                                                                                     | 274                        |
| 95% CI [N]         | 1797 - 1967                                             | 1919 - 2124                    | 984 - 1293                         | 802 - 1215                             | 1070 - 1382                                       | 1096 - 1362                    | 1002 - 1425                                                                                             | 997 - 1301                 |

Different superscript letters indicate significant differences according to 1-way ANOVA, followed by post hoc Scheffé test between veneering groups within 1 aging level, separately





**Fig. 6** Completely exposed PEEK surface after cutting a tested, HIPC veneered FDP

## Discussion

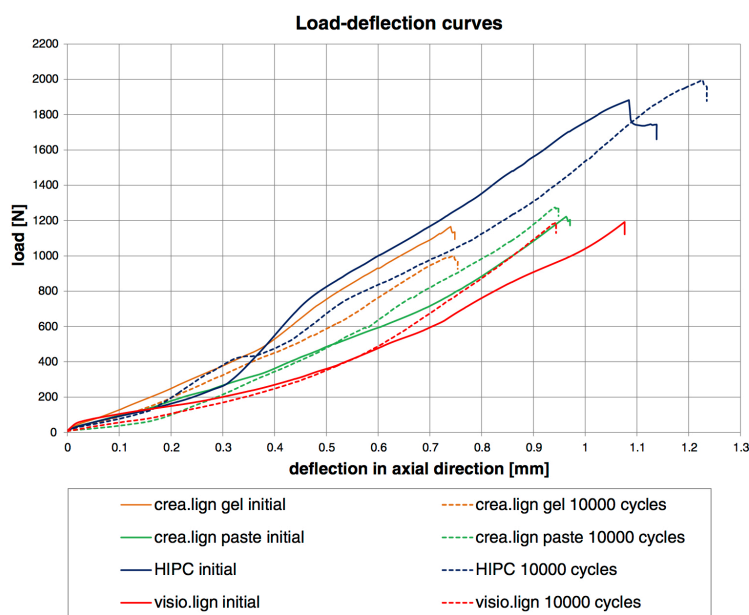
The investigation of the influence of the different veneering methods on the load-bearing capacity was the main goal of this study. Generally, all tested FDPs showed sufficient fracture resistance compared with the anticipated bite force [6], and therefore, both the chosen thickness of the framework and the chosen thickness of the veneering can be recommended. The digitally veneered FDPs showed a higher load-bearing capacity than the three other groups, which were all in the same range. Therefore, the null hypothesis of this study that the veneering method had no influence on the fracture load of PEEK FDPs had to be rejected.

Load deflection curves, one for each group are provided in Fig. 7. One can see that the curves follow in general the same shape characteristics. One exception is the curve for the HIPC (initial) veneer, which showed a slight discontinuity in the gradient between 0.3 and 0.5 mm, which was probably attributable to the adjustment of the tin foil. In general, the curves show a non-linear elastic behavior of the probes. The relationship between the vertical deflection and the force seems therefore to represent a function of higher order. In general, the modulus of elasticity of the veneered FDPs was, however, independent of the veneering and was therefore substantially attributed to the characteristics of PEEK.

The reason for the increased stability of the digital veneering could be, among others, that some complex manual steps in the manufacturing process could be reduced. By this, simply expressed, only the adhesive bonding of the veneer to the framework was the only manual step, whereas in all other veneering methods a variety of error sources in the manufacturing process were excluded. These errors add up and may in the end have a negative impact on stability. A second reason could be the higher level of curing in the pre-manufactured digital veneering compared with conventional manual veneering with veneering composite resin, since this is associated with higher strengths [25].

The modulus of elasticity of the examined veneering materials could also have an influence on the load-bearing capacity. PEEK as a framework has a modulus of elasticity of

**Fig. 7** Load-deflection curves



4.0 GPa. The E-modulus of the used veneering material HIPC was 2.8 GPa, which is together with the visio.lign veneering material, which displayed the lowest modulus of elasticity of all investigated materials. For the veneering materials crea.lign and crea.lign paste, the values accounted for 4.4 and 5.5 GPa, respectively. When veneering with the pre-manufactured visio.lign veneers of lower E-modulus, failure was not within the veneers, but rather in the connector area as with any other veneering material under investigation. This could explain the lower values of the load-bearing capacity with visio.lign veneers as compared to the HIPC veneering. The failure zone was veneered with combo.lign, which had a modulus of elasticity of 8.5 GPa. This has to be considered in upcoming studies and when repairing veneers, this should be carried out with combo.lign whereas the remaining veneer should be replaced with a more elastic material.

In contrast to the challenges mentioned with conventional veneering composite resin [23], no pre-test failures related to thermocycling were observed in this study and the thermocycling had no influence on the load-bearing capacity. The failure type cracking was observed for the first three groups while the fourth group showed an adhesive failure. Nevertheless, the fourth group showed comparable fracture loads to the FDPs with conventional veneering composite resin.

The higher standard deviation of the other three groups compared to the group with digital veneering could be explained by the manual steps in the conventional veneering, since the applied manufacturing process should ensure a high degree of congruence between the outer contour, but slight deviations cannot be entirely excluded, which can be considered as a limitation of this study.

The weak spot in the first three groups of digital and conventional veneering is quite clearly located at the connectors, which is attributed to the smallest thickness of the PEEK framework at these points. Under axial load, regardless of the veneering material, at this position the distortion values are highest, making the fracture load of the veneering material being reached first. In the fourth group, the veneer seems to have a higher strength, so that the adhesive bond fails before the veneer can even break.

The reason for the observed pure adhesive breakdown lies in the pre-treatment. Although the airborne-particle abrasion increases the surface area and allows a better infiltration of the adhesive material, the bonding is still predominantly characterized by mechanical interactions between the PEEK surface and the adhesive material. In contrast to this, the veneering material is additionally bonded by chemical means to the adhesive visio.link layer and therefore creates a stronger bonding in all cases investigated in this study.

In the presented results, one must take into account that the model material CoCrMo has a much higher elastic modulus than the hard tooth tissue. Furthermore, the physiological

tangential movement of the abutment teeth in the experiment is not modeled and therefore the fracture test allows comparison between the different veneering materials but has limited clinical relevance.

Before clinical studies are carried out, further studies should model the physiological mobility of natural teeth using a periodontal ligament as well as the E-modulus of the dental hard tooth tissue of the actual abutment teeth, expecting lower values of the fracture load. Also an investigation of the combination of pre-treatment using airborne-particle abrasion with different particle size and acids is of major interest. In addition, the fracture load of different digital veneering materials on PEEK frameworks could be subject of a next study.

## Conclusions

PEEK may be a suitable material for removable prostheses when considering the results of this study. However, long-term investigations and advancement of PEEK CAD/CAM processing are still warranted. Apart from the advantages resulting from the industrial production on a large scale as resistance against wear, standardized polymerization and a relatively low discoloration potential, veneering using CAD/CAM method result in a lower monomer content, which implies the biggest advantage over the manual veneering in future clinical use.

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**Informed consent** For this type of study, formal consent is not required.

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**2.2 Originalarbeit: Stawarczyk B, Taufall S, Roos M, Schmidlin PR, Lümke M. Bonding of composite resins to PEEK: the influence of adhesive systems and air-abrasion parameters. Clin Oral Investig 2018;22(2):763-771 (Impact factor 2016: 2,308)**

***Zusammenfassung:***

Ziel: Der Schwerpunkt der vorliegenden Untersuchung war, den Einfluss von unterschiedlicher Oberflächenvorbehandlung und unterschiedlichen Konditionierungsverfahren auf die Zugverbundfestigkeit zwischen Verblendkunststoff zu Polyetheretherketon (PEEK) zu untersuchen.

Material und Methode: Vierhundert PEEK-Prüfkörper wurden mit den folgenden Sandstrahlparametern ( $n_1 = 80$  / Vorbehandlung) vorbehandelt: (i)  $50\text{ }\mu\text{m Al}_2\text{O}_3$  (0,05 MPa); (ii)  $50\text{ }\mu\text{m Al}_2\text{O}_3$  (0,35 MPa); (iii)  $110\text{ }\mu\text{m Al}_2\text{O}_3$  (0,05 MPa); (iv)  $110\text{ }\mu\text{m Al}_2\text{O}_3$  (0,35 MPa); und (v) Rocatec  $110\text{ }\mu\text{m}$  (0,28 MPa). Diese Vorbehandlungen wurden mit den folgenden Konditionierungen kombiniert ( $n_2 = 20$  / Vorbehandlung / Konditionierung): (a) visio.link (VL); (b) Monobond Plus / Heliobond (MH); (c) Scotchbond Universal (SU); und (d) Dialog Bonding Fluid (DB). Nach Verblenden aller Prüfkörper mit Dialog Okklusal und Altern (28 Tage  $\text{H}_2\text{O}$ ,  $37\text{ }^\circ\text{C}$  + 20,000 thermischen Zyklen,  $5/55\text{ }^\circ\text{C}$ ) wurde die Zugverbundfestigkeit gemessen. Die Daten wurden anschließend unter Verwendung der Kaplan-Meier-Überlebensanalyse mit Breslow-Gehan Test und Cox-Regression ausgewertet.

Ergebnisse: Die größte Auswirkung auf die Zugverbundfestigkeitswerte zeigte die Art der Konditionierung, gefolgt vom Strahlendruck bei der Vorbehandlung, während die Partikelgröße des Strahlmittels keinen Einfluss zeigte. Die Prüfkörper, die bei 0,35 MPa gestrahlt wurden hatten die höchste Überlebensrate, wobei dieses Verhalten innerhalb der Gruppe mit VL-Konditionierung statistisch nicht signifikant war. Innerhalb der mit MH konditionierten Gruppe, zeigte die Vorbehandlung unter Verwendung von  $110\text{ }\mu\text{m Al}_2\text{O}_3$  bei einem Strahlendruck

von 0,05 MPa gegenüber den Gruppen, die mit 50  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  bzw. 110  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  bei 0,35 MPa Strahlruck vorbehandelt wurden höhere Überlebensraten. Die Verwendung von VL zeigte mit Zugverbundfestigkeitswerten, die unabhängig von der Vorbehandlung höher als 25 MPa waren, die höchste Überlebensrate unter den Adhäsivsystemen. Als einzige Ausnahme zeigte VL signifikant höhere Überlebensraten verglichen mit der MH-Konditionierung.

Schlussfolgerung: Die Wahl des Adhäsivsystems und die Nutzung hoher Strahlrücke beim Partikelstrahlen als Vorbehandlung erhöhen die Zugverbundfestigkeit zwischen PEEK und dem Verblendkunststoff, während die mittlere Korngröße des Strahlgutes einen vernachlässigbaren Einfluss hat.

Klinische Relevanz: Nach den Ergebnissen der vorliegenden Untersuchung kann der beste adhäsive Verbund zwischen PEEK und dialog occlusal unter Konditionierung der Oberfläche mit viso.link und einer Vorbehandlung mit Korrundstrahlen bei einem Strahlruck von 0,35 MPa erreicht werden.





## Bonding of composite resins to PEEK: the influence of adhesive systems and air-abrasion parameters

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### Abstract

**Objective** The objective of the study was to investigate the tensile bond strength (TBS) to polyaryletheretherketone (PEEK) after different pretreatment and conditioning methods.

**Methods** Four hundred PEEK specimens were fabricated and allocated to the following air-abrasion methods ( $n_1 = 80$ /pretreatment): (i) 50  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  (0.05 MPa); (ii) 50  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  (0.35 MPa); (iii) 110  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  (0.05 MPa); (iv) 110  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  (0.35 MPa); and (v) Rocotec 110  $\mu\text{m}$  (0.28 MPa). These pretreatments were combined with the following conditioning methods ( $n_2 = 20$ /pretreatment/conditioning): (a) visio.link (VL); (b) Monobond Plus/Heliobond (MH); (c) Scotchbond Universal (SU); and (d) dialog bonding fluid (DB). After veneering of all specimens with dialog occlusal and aging (28 days  $\text{H}_2\text{O}$ , 37 °C + 20,000 thermal cycles, 5/55 °C), TBS was measured. Data was analysed using Kaplan–Meier survival analysis with Breslow–Gehan test and Cox-regressions.

**Results** The major impact on TBS showed the conditioning, followed by the air-abrasion-pressure, while the grain size of the air-abrasion powder did not show any effect. Specimens air-abraded at 0.35 MPa showed the highest survival rates.

However, within VL groups, this observation was not statistically significant. Within MH groups, pretreatment using 110  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  and 0.05 MPa resulted in higher survival rates compared to groups treated with 50 and 110  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  using a pressure of 0.35 MPa. The use of VL showed the highest survival rates between the adhesive systems and the TBS values higher than 25 MPa independent of the pretreatment method. As an exception, only VL showed significantly higher survival rates when compared to MH.

**Conclusions** The adequate choice of the adhesive system and higher pressures improved the TBS between PEEK and veneering resin composite. The particle size had no major impact.

**Clinical relevance** According to this study, best veneering of PEEK with dialog occlusal can be achieved by conditioning with visio.link in combination with the pretreatment of airborne particle abrasion at a pressure of 0.35 MPa.

**Keywords** Tensile bond strengths · Failure type · PEEK · Veneering resin composite · Airborne particle abrasion

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### Introduction

There is a great interest and ongoing research with regard to substitute materials, which show similar mechanical characteristics like human bone. Metal is one of the materials which is already substituted by polyaryletherketones (PAEK). This substitute material is already used within industrial applications and generally characterized by their high mass-based stability, strong resistance against temperature loads, chemical and physical stress, and corrosion [1]. The materials, which are currently mainly used in medicine, are polyaryletherketoneetherketoneketone (PEKEKK), polyetherketoneketone (PEKK), and polyaryletheretherketone (PEEK) [2]. These materials are

additionally characterized by high stabilities against chemical and radiological stresses, where especially PEEK is known for outstanding mechanical properties. PEEK is a high temperature polymer and semi-crystalline thermoplastic, which consists of an aromatic ring with functional groups interconnected by ketones of the previously named group of PAEKs [3–5]. Due to the outstanding properties in combination with its outstanding biocompatibility and the high stability similar to human bone, the material is used in a variety of applications in the medical field such as spine implants or bone substitute for large defects where autologous bone excretes [7, 8].

Due to the characteristics mentioned above, PEEK became very interesting for applications in dentistry as well. The types of applications in dentistry are also manifold but primarily PEEK is used for the fixed dental prosthetic framework (FDP) or the removable partial denture abutment framework [9]. The fact that the material shows excellent milling and grinding properties [6] is advantageous with respect to the possibility of enlarging the field of indications for PEEK and underlines the potential of the material in dentistry. Previous studies have already shown that PEEK is well processable by computer-aided design/computer-aided manufacturing (CAD/CAM), because lower deformations and higher fracture loads can be achieved compared to other processes [10]. Besides to all these positive aspects; however, it has to be mentioned that the material has an unaesthetic grey colour and appears opaque. Therefore, an additional veneering, at least in the visible area, is indispensable to overcome this rather unaesthetical drawback.

For that reason, various studies have been carried out to investigate the bond strength between PEEK frameworks and resin composites depending on different pretreatments [5, 6, 11–19]. In these studies, the pretreatments had been performed by the use of airborne particle abrasion, treating the surface with piranha-etching [13–16], sulphuric acid [5, 6, 12, 17], or different types of plasma [18, 20]. Moreover, different adhesive systems for a surface conditioning after pretreatment have been studied in detail [11, 14–16, 21, 22]. Based on these studies, airborne-particle abrasion could be recommended as one of the best initial pretreatment options of PEEK surfaces. However, it is striking that in particular, the adjustable and varying parameters of this process such as blasting pressure and the powder particle grain size of the blasting material have not been studied in detail yet. Moreover, the effect of different adhesive systems as a subsequent treatment and conditioning step after air-abrasion is of big interest, as the chemical mechanism is still questionable in order to achieve a durable bonding.

Therefore, this study was focusing on the influence between five different types of pretreatments in terms of airborne-particle abrasion with varying pressure and particle sizes in combination with four different adhesive systems on the tensile bond strength (TBS) values between PEEK and veneering material. These data will help to improve the TBS

in the clinical application and thus achieve a higher durability and lower failure probability.

In general, several test methods can be used to describe the bond properties including the well-known shear bond tests and tensile bond strength tests or even newer and more accurate test methods, such as microshear and microtensile tests [23]. Both micromethods resulted in higher bond strength values due to the smaller bonding area, but at the same time, these methods are very technique-sensitive and elaborate in comparison to the macro-test methods [24, 25]. However, macro-test methods are more commonly used [24, 25]. Therefore, macro-bond strength test was applied due to their direct and quick results being achieved, as well as their ease of handling [25]. To obtain clinically relevant statements, specimens underwent an artificial aging in a thermocycler. Thermocycling simulates temperature changes in the oral cavity during a certain period of time [26, 27].

The null hypothesis of this study was that neither the pretreatment (particle grain size and pressure) nor the type of adhesive system nor the combination of both has an influence on the TBS between the PEEK and the used veneering resin composite.

## Materials and methods

In order to perform the TBS tests, a blinded operator cut 400 specimens with a square crosscut of  $10 \times 10 \times 3$  mm out of PEEK blanks (Tizian PEEK, Schütz Dental, Rosbach, Germany). This substrate material has been selected because it consists of pure/unfilled PEEK without additional filler particles. This avoids differences in the surface microstructure of the specimens, and thus, comparable results of the tensile bond strengths between the different bonding agents can be achieved.

PEEK specimens were embedded in a self-cured acrylic resin (ScandiQuick, ScanDia, Hagen, Germany) and grinded with silicone carbide papers (SiC) up to P500 (Tegamin-20, Struers, Ballerup, Denmark). Subsequently, the polished specimens were randomly divided into 20 randomized combinations between pretreatment and conditioning of the PEEK surface (Fig. 1). All used materials are presented in Table 1. Specimens were air-abraded at a distance of 10 mm (basic Quattro IS; Renfert, Hilzingen, Germany) in an angle of  $45^\circ$  between the nozzle and the specimen surface. The silica coated groups were air-abraded at an angle of  $90^\circ$ . Immediately after air-abrasion, the conditioning was performed using different adhesive systems, which are described in Table 1. In general, the chosen systems are a crosscut through the most frequently used systems in dentistry. The thoughtful choice was based on the differences in chemical composition following previous published results and concentrates on the impact of different components on tensile bond strength to gain new scientific findings.

**Fig. 1** Study design: overview of all tested groups

| Substrate                                          | preconditioning                                                                                                    | Adhesive system | composite                  |
|----------------------------------------------------|--------------------------------------------------------------------------------------------------------------------|-----------------|----------------------------|
| PEEK (Tizian PEEK)<br>10mm x 10mm x 3mm<br>(N=400) | $\varnothing = 50 \mu\text{m}$ , pressure = 0.05 MPa<br>(n=80)                                                     | VL (n=20)       | dialog occlusal<br>(N=400) |
|                                                    |                                                                                                                    | SU (n=20)       |                            |
|                                                    |                                                                                                                    | MH (n=20)       |                            |
|                                                    |                                                                                                                    | DB (n=20)       |                            |
|                                                    | $\varnothing = 50 \mu\text{m}$ , pressure = 0.35 MPa<br>(n=80)                                                     | VL (n=20)       |                            |
|                                                    |                                                                                                                    | SU (n=20)       |                            |
|                                                    |                                                                                                                    | MH (n=20)       |                            |
|                                                    |                                                                                                                    | DB (n=20)       |                            |
|                                                    | $\varnothing = 110 \mu\text{m}$ , pressure = 0.05 MPa<br>(n=80)                                                    | VL (n=20)       |                            |
|                                                    |                                                                                                                    | SU (n=20)       |                            |
|                                                    |                                                                                                                    | MH (n=20)       |                            |
|                                                    |                                                                                                                    | DB (n=20)       |                            |
|                                                    | $\varnothing = 110 \mu\text{m}$ , pressure = 0.35 MPa<br>(n=80)                                                    | VL (n=20)       |                            |
|                                                    |                                                                                                                    | SU (n=20)       |                            |
|                                                    |                                                                                                                    | MH (n=20)       |                            |
|                                                    |                                                                                                                    | DB (n=20)       |                            |
|                                                    | rocathec method (tribochemical silicatisation);<br>$\varnothing = 110 \mu\text{m}$ , pressure = 0.28 MPa<br>(n=80) | VL (n=20)       |                            |
|                                                    |                                                                                                                    | SU (n=20)       |                            |
|                                                    |                                                                                                                    | MH (n=20)       |                            |
|                                                    |                                                                                                                    | DB (n=20)       |                            |

The adhesive systems visio.link and dialog bonding fluid both contain methyl-methacrylate (MMA) monomer, while visio.link contains pentaerythritol triacrylate (PETIA) as well. In contrast, dialog bonding fluid contains urethane dimethacrylate (UDMA). Scotchbond Universal is a universal adhesive, which was originally and in theory developed for all restoration materials. It contains 10-methacryloyloxydecyl-dihydrogenphosphat (MDP) monomer and silane and further dimethacrylate in a one bottle approach. In contrast, Monobond Plus and Heliobond represents a two step adhesive system. Monobond Plus is a silane coupling agent with phosphoric acid methacrylate and sulphide methacrylate. Phosphoric acid methacrylate shows good bonding to oxide ceramic and sulphide methacrylate to alloys. However, in this study, the tested PEEK material was unfilled. The associated Heliobond has the task to create a bonding between the silane-coupling agent Monobond Plus and the composite (in this study veneering resin composite). It contains dimethacrylate, such as bisphenol-A diglycidyl ether dimethacrylate (Bis-GMA) and triethylene glycol dimethacrylate (TEGDMA).

Acrylic cylinders with an inner diameter of 2.9 mm and a length of 10 mm were filled with veneering resin composite (dialog occlusal, Schütz Dental) and polymerized for 360 s in a laboratory curing division bre.Lux PowerUnit (intensity 220 mW/cm<sup>2</sup>, bredent, Senden, Germany). All specimens were stored in distilled water for 28 days at 37 °C and then

thermocycled (thermocycler THE 1100; SD Mechatronics, Feldkirchen-Westerham, Germany) between 5 and 55 °C with a dwell time of 20 s for 20,000 cycles.

TBS measurements were carried out in a standardized machine (Zwick 1445; Zwick, Ulm, Germany). The polymerized acrylic cylinder was fixed into the holding device of the testing machine and pulled with a crosshead speed of 5 mm/min until the adhesive bond failed. TBS was calculated according to the following equation:  $s = F/A$  ( $s$ : tensile bond strength [MPa],  $F$ : load at fracture [N],  $A$ : adhesive area [mm<sup>2</sup>]). The failure types were analysed under a stereomicroscope with 50" magnification (Carl Zeiss Axioskop 2 MAT, Zeiss Mikroskopie, Göttingen, Germany) after debonding and classified as follows: (i) adhesive between PEEK substrate and veneering resin composite; (ii) cohesive in the veneering resin composite; and (iii) cohesive in PEEK substrate.

The measured data was coded in Excel 2010 (Microsoft Corporation; Redmond, WA, USA) and analysed statistically with SPSS Version 23.0 (IBM, SPSS, Statistics, Armonk, NY, USA). Specimens, which showed debonding during thermal cycling and did not survive the aging processes were assigned a TBS value equal to 0 MPa and acted as prefailures. Descriptive statistics such as mean, standard deviation (SD), and 95% confidence intervals were computed. For quantitative variables, the assumption of normality was tested with the Kolmogorov–Smirnov test. The general linear model analysis



**Table 1** Summary of used products, compositions, manufacturers, and the application steps

| Material            | Product Name         | Abbreviation | Manufacturer                            | Application steps as recommended by the manufacturer                                                                                                             | Composition                                                                          | Lot No.       | Curing light used                                                               |
|---------------------|----------------------|--------------|-----------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|---------------|---------------------------------------------------------------------------------|
| Adhesives           | visio.link           | VL           | breident, Senden, Germany               | 1. Apply adhesive on the PEEK surface with a brush<br>2. Light cure for 90 s (bre.Lux PowerUnit, intensity 220 mW/cm <sup>2</sup> , breident, Senden, Germany)   | MMA, PETIA (pentaerythritol--triacrylate), photoinitiators                           | 114,784       | bre.Lux PowerUnit, intensity 220 mW/cm <sup>2</sup> , breident, Senden, Germany |
|                     | Scotchbond Universal | SU           | 3 M, Seefeld, Germany                   | 1. Apply with disposable applicator and rub it in for 20 s<br>2. Subsequently direct a gentle stream of air over the liquid for about 5 s<br>Light cure for 10 s | MDP phosphate monomer, DM, HEMA, Vitrebond copolymer, filler, ethanol, water, silane | 521,215       | Elipar Freelight 2, 1200 mW/cm <sup>2</sup> , 3 M, Seefeld, Germany             |
|                     | Monobond Plus        | MH           | Ivoclar Vivadent, Schaan, Liechtenstein | 1. Apply with a microbrush for 60 s<br>2. Disperse dry remaining excess with a strong stream of air                                                              | Silane methacrylate, phosphoric acid methacrylate, sulphide methacrylate             | S14727        | –                                                                               |
|                     | Heliobond            |              |                                         | 1. Apply it for 15–30 s<br>2. Carefully rinse with water and dry with a stream of water- and oil-free air                                                        | Bis-GMA, TEGDMA                                                                      | R22281        | Elipar Freelight 2, 1200 mW/cm <sup>2</sup> , 3 M, Seefeld, Germany             |
| Veneering composite | Dialog Bonding Fluid | DB           | Schütz Dental, Rosbach, Germany         | Light cure for 10 s<br>1. Apply with a brush<br>Light cure for 90 s                                                                                              | MMA, UDMA, photoinitiators                                                           | 2,014,008,056 | bre.Lux PowerUnit, intensity 220 mW/cm <sup>2</sup> , breident, Senden, Germany |
|                     | Dialog Occlusal      |              |                                         | Light cure for 360 s                                                                                                                                             | UDMA, Bis-GMA, 1,4-butane dioldimethacrylate                                         | 2,014,009,689 | bre.Lux PowerUnit, intensity 220 mW/cm <sup>2</sup> , breident, Senden, Germany |

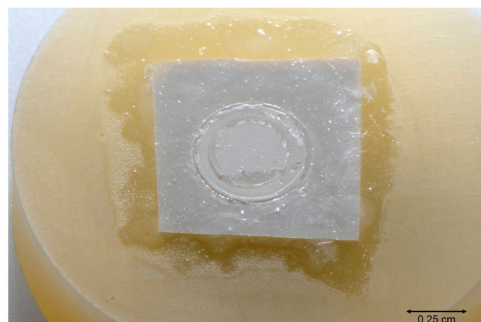
MMA methyl methacrylate, Bis-GMA bisphenol-A diglycidyl ether dimethacrylate, TEGDMA triethylene glycol dimethacrylate, UDMA urethane dimethacrylate, HEMA hydroxyethylmethacrylate, DM dimethacrylate, MDP 10-methacryloyloxydecyl-dihydrogenphosphat

was performed. Unfortunately, inclusion of prefailures in the analysis can underestimate the true TBS. An alternative approach for statistical analysis is to treat the TBS values for prefailed specimens as censored and actually measured TBS values as non-censored observations. In this setting, the Kaplan–Meier survival estimates, the Breslow–Gehan tests, and the Cox-regressions for the TBS of non-censored and censored data were computed. The results of statistical analyses with  $p$  values less than 0.05 were interpreted as statistically significant.

## Results

The descriptive statistics are summarized in Table 2. The highest influence on the TBS was exerted by the use of an adhesive system (partial eta squared  $\eta_p^2 = 0.510$ ,  $p < 0.001$ ) followed by the pressure during the air-abrasion ( $\eta_p^2 = 0.306$ ,  $p < 0.001$ ), while the grain size of the air-abrasion powder did not show a significant effect ( $p = 0.072$ ). The effect of the binary, ternary, and quaternary combinations of the three parameters was also significant for the combinations: adhesive system coupled with grain size ( $\eta_p^2 = 0.043$ ,  $p = 0.001$ ), adhesive system coupled with pressure ( $\eta_p^2 = 0.225$ ,  $p < 0.001$ ), and adhesive system coupled with grain size and coupled with pressure ( $\eta_p^2 = 0.028$ ,  $p = 0.017$ ).

Kolmogorov–Smirnov indicated that the data were not normally distributed because the tests were significant for 11 of 20 (55%) subgroups ( $\alpha = 0.05$ ). In addition, many subgroups showed prefailed specimens during the aging process showing the adhesive failure type (Fig. 2, Table 3). Also, significant differences were found in the number of prefailed specimens ( $p < 0.001$ , chi-square test). Therefore, the prefailed specimens, which occurred during the aging with thermal cycling, were treated as censored and the actually measured TBS values as non-censored observations. Reports of the median survival TBS given by Kaplan–Meier survival were observed in different test groups. In summary, the lowest survival rates were observed for MH.



**Fig. 2** Picture of adhesive failure type

## Impact of pretreatment

Within visio.link (VL) groups, no statistical impact of pretreatment on the survival was observed ( $p = 0.093$ ). Within Scotchbond Universal (SU) and dialog bonding fluid (DB) groups, air-abraded specimens with a pressure of 0.35 MPa showed significantly higher survival rates as compared to specimens, which were treated at 0.05 MPa. The same could be observed for specimens, which were treated with silica-modified corundum particles, regardless of the  $\text{Al}_2\text{O}_3$  mean particle size (SU and DB  $p < 0.001$ ). Within MH groups, pretreatment using 110  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  and a pressure of 0.35 MPa resulted in higher survival rates compared to groups treated by using 50 and 110  $\mu\text{m}$   $\text{Al}_2\text{O}_3$ , with 0.05 MPa pressure ( $p = 0.002$ ).

## Impact of adhesive system

Within specimens treated with 50 and 110  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  and a pressure of 0.05 MPa as well as specimens coated silica-modified corundum particles, VL showed the highest survival rates compared to the remaining adhesive systems ( $p < 0.001$ ). Within specimens treated with 50  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  and 0.35 MPa pressure, VL ranged within the same values as the other

**Table 2** Overview of descriptive statistics included mean, standard deviation (SD), and 95% confidence interval (95%CI) for TBS values divided into the different pretreatment and preconditioning

| Pretreatment                                      | VL                            |              | SU                             |              | MH                             |             | DB                              |              |
|---------------------------------------------------|-------------------------------|--------------|--------------------------------|--------------|--------------------------------|-------------|---------------------------------|--------------|
|                                                   | Mean (SD)                     | 95% CI       | Mean (SD)                      | 95% CI       | Mean (SD)                      | 95% CI      | Mean (SD)                       | 95% CI       |
| $\text{Al}_2\text{O}_3$ 50 $\mu\text{m}$ 0.5 bar  | 28.58 (6.27)                  | [25.6; 31.6] | 10.58 (9.09) <sup>a</sup> {4}  | [6.3; 14.9]  | 1.57 (4.28) <sup>a</sup> {16}  | [-0.5; 3.6] | 1.80 (4.46) <sup>a</sup> {17}   | [-0.3; 3.9]  |
| $\text{Al}_2\text{O}_3$ 50 $\mu\text{m}$ 3.5 bar  | 26.61 (5.69)                  | [23.9; 29.3] | 29.52 (52.9)                   | [26.1; 33.0] | 5.90 (10.50) <sup>a</sup> {15} | [0.9; 10.9] | 27.86 (6.12)                    | [24.9; 30.8] |
| $\text{Al}_2\text{O}_3$ 110 $\mu\text{m}$ 0.5 bar | 29.82 (8.64) <sup>a</sup> {1} | [25.7; 33.9] | 5.83 (79.49) <sup>a</sup> {13} | [1.6; 10.0]  | 2.28 (5.68) <sup>a</sup> {17}  | [-0.4; 5.0] | 12.20 (8.01) <sup>a</sup> {4}   | [8.4; 16.0]  |
| $\text{Al}_2\text{O}_3$ 110 $\mu\text{m}$ 3.5 bar | 28.24 (5.36)                  | [25.7; 30.8] | 25.76 (7.92)                   | [22.0; 29.5] | 12.68 (12.01) <sup>a</sup> {8} | [7.0; 18.3] | 28.52 (5.59)                    | [25.8; 31.2] |
| Rocatec                                           | 29.61 (7.72)                  | [25.9; 33.3] | 20.44 (8.28)                   | [16.5; 24.4] | 5.96 (8.51) <sup>a</sup> {13}  | [1.9; 10.0] | 17.83 (12.69) <sup>a</sup> {15} | [11.8; 23.8] |

All values are listed in megapascal

<sup>a</sup> Not normally distributed groups {number of prefailed specimens in curly braces}

**Table 3** Median survival TBS and 95% confidence interval (95%CI) of survival in all subgroups

| Pretreatment                                  | VL     |              | SU     |              | MH     |              | DB     |              |
|-----------------------------------------------|--------|--------------|--------|--------------|--------|--------------|--------|--------------|
|                                               | Median | 95% CI       | Median | 95% CI       | Median | 95% CI       | Median | 95% CI       |
| Al <sub>2</sub> O <sub>3</sub> 50 µm 0.5 bar  | 28.0   | [26.0; 29.1] | 15.3   | [6.5; 24.0]  | 3.6    | [0; 10.1]    | 13.2   | [6.5; 19.8]  |
| Al <sub>2</sub> O <sub>3</sub> 50 µm 3.5 bar  | 26.8   | [21.3; 32.1] | 30.9   | [20.5; 41.3] | 23.6   | [21.9; 25.3] | 29.7   | [25.0; 34.4] |
| Al <sub>2</sub> O <sub>3</sub> 110 µm 0.5 bar | 31.1   | [28.8; 33.3] | 17.4   | [5.1; 29.6]  | 15.9   | [8.7; 23.0]  | 15.2   | [7.8; 22.4]  |
| Al <sub>2</sub> O <sub>3</sub> 110 µm 3.5 bar | 28.2   | [27.0; 29.2] | 26.4   | [23.8; 28.9] | 22.0   | [11.8; 32.1] | 27.4   | [25.7; 29.0] |
| Rocatec                                       | 30.9   | [29.9; 31.8] | 20.0   | [13.2; 26.7] | 17.4   | [15.3; 19.4] | 25.8   | [22.0; 29.4] |

All values are listed in megapascal

adhesive systems ( $p = 0.06$ – $0.463$ ). Within 110 µm and 0.35 MPa, VL showed significantly higher survival rates than MH ( $p = 0.15$ ). No differences were observed between VL and SU ( $p = 0.711$ ) as well as DB ( $p = 0.718$ ).

### Fracture types

All specimens showed adhesive fractures (Fig. 2).

### Discussion

The research focus of bonding properties between framework and veneering materials using different pretreatments and conditioning methods is increasing, especially when it comes to new materials such as PEEK. Previous studies showed that an increase of the surface area achieved by airborne-particle abrasion and the use of MMA-containing adhesive systems leads to the improvement of the bonding characteristics of PEEK [11, 14–16, 21]. To the best of our knowledge, the influence of the individual parameters of the air-abrasion process (particle grain size and pressure) has not been studied in PEEK materials yet. That is why this study focused on the influence between the pretreatment with varying parameters such as particle size and the applied pressure in combination with the use of different adhesive systems.

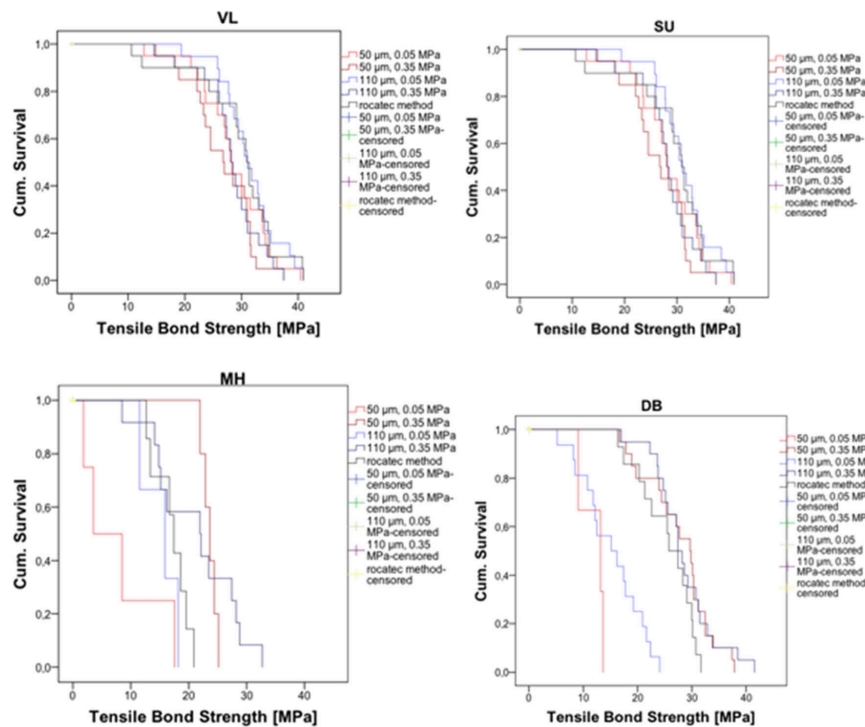
In general, the use of PEEK in dentistry as a framework material for FDPs requires a permanently stable and durable bonding to veneering materials. Based on the achieved results, the hypothesis of this study had to be rejected in all cases. In summary, the present study showed that the adhesive systems had a strong effect on the bonding properties between PEEK and veneering composite resin. The air-abrasion parameters also influenced the TBS, whereby the pressure showed an impact on the bonding characteristics, in contrast to the grain size. Also, the adhesive systems Scotchbond Universal and dialog bonding fluid achieved very good bonding properties with increased air-abrasion pressure, while the use of lower pressure resulted in lower values of TBS, respectively. In case of higher air-abrasion pressure, the values were comparable to

those of the well-investigated adhesive system visio.link. In the present study, visio.link acted as the positive control group, because all previous studies showed very high bonding properties after the use of visio.link as conditioner on different pretreated PEEK surfaces [11, 14–16]. Also, the survival rates of groups conditioned using visio.link showed the most favourable results so far. For the non-parametric approach, the Kaplan–Meier estimates of the cumulative failure distribution function (Fig. 3) and the robust estimates for median failure estimates were provided (Table 3). This non-parametric analysis not only correctly handles the violation of normality but also correctly adjusts the second difficulty in the data pertain to prefailures. Inclusion of prefailures in the parametric analysis can underestimate the true TBS. The Kaplan–Meier analysis correctly treats the values for prefabricated specimens as censored and uses the actual measured values as non-censored observations. Estimation of the cumulative failure distribution function runs in statistics under a general name of the survival analysis. Frequently, survival time is assumed in applications. Maybe it is less well known that the non-parametric Kaplan–Meier methodology is very useful for analysis of other primary outcomes subject to censoring, where the survival time is replaced by, for example, the TBS, i.e., the amount of stress necessary to destroy a specimen.

When looking at the composition of visio.link and dialog bonding fluid, it can be suggested that the component PETIA has a high capacity to modify the PEEK surface, also because visio.link consequently provided even higher bonding properties to PEEK restorations.

The low TBS values of the Monobond Plus/Heliobond system over all pretreatments in this study could be attributed to the tested PEEK material, which was unfilled; thus, no elements were available to which the Monobond Plus was able to chemically dock to.

Since Scotchbond Universal (one-bottle system) leads to higher bonding properties, it can be assumed that the two-bottle system may be prone to errors. It is also conceivable that the immediate contact of the PEEK surface with the dimethacrylate increases the bonding properties. By the use



**Fig. 3** Cumulative survival function for prefabricated and non-prefabricated specimens with respect of TBS [MPa] by Kaplan-Meier. **a** VL. **b** SU. **c** MH. **d** DB

of Monobond Plus/Heliobond adhesive system, the PEEK surface is first confronted with the silane coupling agent. Moreover, it is also conceivable that Scotchbond Universal contains other substances, that are on the one hand not named by the manufacturer and on the other hand not known yet to promote the connection to air-abraded PEEK surfaces.

During the experiments of this study, it was detected that the PEEK surface properties were changed within a few minutes after performing the pretreatment by air-abrasion. A longer waiting period after the air-abrasion process resulted in lower TBS values than for specimens which had been veneered immediately after pretreatment. One possible explanation for this observation could be the surface moisture. Air-abrasion, especially with high-pressure values, leads to high temperatures on the PEEK surface, and additionally, the surface is exposed to a very dry air stream. After some time, the surface again undergoes the ambient moisture. Since the methacrylates in the adhesive systems are hydrophobic, this could strongly influence the bond strength. Therefore, the study was stopped and all specimens were air-abraded, conditioned, and veneered immediately. Referring this to the results, the first conclusion, which can be drawn, is that an

immediate and continuous workflow—regarding to the steps of pretreatment, conditioning and veneering—is one important aspect, which should be considered in order to achieve good bonding properties to any air-abraded PEEK surface. Moreover, this recommendation can be expanded by the fact that PEEK frameworks should be air-abraded with a high pressure.

In this study, the used macro-tensile test resulted in adhesive failure types of specimens only, after measurements. Therefore, we can state that only the bond strength was measured. The mechanical internal properties of the veneering resin composite are not included in the TBS values. In contrast, shear bond tests often show cohesive failure types and therefore it is supposed that not only the bond strength but more also the overall stability is measured using this method.

Regarding to the design of this study, it has to be pointed out that the manufacturing of the specimens was based on the clinical process in order to achieve the transferability of the results to the clinical field, which had not been taken into consideration in previous studies. Due to the manual preparation of PEEK, specimens showed a realistic statistical scattering.



By manually clamping the specimens in the sample holder, small variations may have occurred with regard to the pulling direction during the tests. These were estimated to be within the range of 3°, resulting in a negligible systematic error of 0.13%. In order to simulate the clinical situation, thermal cycling as aging procedure was used. Thermal cycling is generally used to imitate the commonly changing temperatures in the oral environment. These thermal changes may induce a reduction of bond strength [27]. In contrast, other studies showed an increase of bonding properties after aging, claiming that it supports the post-polymerization process [19]. Due to the undetermined formal estimation of the quantity of intraoral temperature changes, an arbitrary reference of 10,000 thermal cycles represents one service year [26]. In this study, the specimens were thermally cycled for 20,000 cycles. This corresponds to approximately 2 years. In summary, the results of this study therefore represent clinically relevant results. Correct pretreatment and the selection of a suitable adhesive system significantly improved adhesive bonding values, and hence, durability can be achieved. Both the dentist and the technician have to adhere exactly to the given processing. Both the surface processing in the laboratory and chairside play a decisive role in the insertion of the finished prosthetic work and in the choice of a suitable adhesive system. The object of future studies should be, on the one hand, the observed phenomenon of weakening of the bonding in case of a non-simultaneous preparation of the bonding after pretreatment of the surface, and on the other hand, the influence of different pretreatments and the use of different adhesive systems on the adhesive bond to the prepared tooth in clinical use should be investigated. However, a clinical trial with a controlled standardized study design should evaluate the clinical long-term performance as well.

## Conclusions

Within the limitations of the present study, the following conclusions can be drawn:

- The adhesive systems must be carefully chosen based on their composition.
- The conditioning using VL showed the highest TBS values and the smallest number of prefailured specimens compared to the remaining adhesive systems.
- After air-abrasion with pressure of 0.35 MPa Scotchbond Universal and dialog bonding fluid could achieve TBS values compared to the values using visio.link.
- Monobond Plus with Heliobond showed the lowest TBS values and the largest number of prefailured specimens.
- Specimens air-abraded with 0.35 MPa showed the highest TBS values compared with lower pressure values.
- The grain size of the air-abrasion powder particle did not show an effect on the TBS.

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**Compliance with ethical standards** All procedures performed in studies involving human participants are in accordance with the ethical standards of the institutional and/or national research committee and with the 1964 Helsinki Declaration and its later amendments or comparable ethical standards.

**Conflict of interest** The authors declare that they have no conflict of interest.

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**Ethical approval** This article does not contain any studies with human participants or animals performed by any of the authors.

**Informed consent** For this type of study, formal consent is not required.

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### 3 Diskussion

Hier werden die Ergebnisse der in den oben genannten Publikationen durchgeführten Untersuchungen kritisch diskutiert.

#### 3.1 Bruchlast und Versagensart von unterschiedlich verblendetem festsitzenden Zahnersatz auf Basis von PEEK

Die Untersuchung des Einflusses verschiedener Verblendmethoden auf die Bruchlast war das Ziel dieser Untersuchung. Im Allgemeinen zeigten alle getesteten Prüfkörper ausreichend hohe Bruchlasten im Vergleich zur erwarteten Kaufkraft [6] und können daher sowohl in Bezug auf die gewählte Geometrie des Gerüsts, als auch auf die gewählte Wandstärke der Verblendung empfohlen werden. Die digital verblendeten Brücken wiesen eine höhere Bruchlast auf als die drei anderen Gruppen, deren Bruchlastwerte alle in der gleichen Größenordnung gemessen wurden. Daher konnte die Nullhypothese dieser Studie, dass die Verblendungsmethode keinen Einfluss auf die Bruchlast von festsitzendem, verblendetem Zahnersatz auf einem PEEK-Gerüst hat widerlegt werden.

Die Untersuchung der Last-Auslenkungs-Kurven zeigte, dass diese mit Ausnahme der Kurve für die HIPC-Verblendung ohne Alterung alle einem korrelierten Verlauf folgen. Bei der HIPC-Verblendung ohne Alterung konnte eine leichte Diskontinuität im Gradienten zwischen 0,3 und 0,5 mm Auslenkung identifiziert werden, was vermutlich auf die Anpassung der Zinnfolie an den Prüfstempel zurückzuführen ist. Im Allgemeinen zeigen die Kurven ein nichtlineares elastisches Verhalten der Prüfkörper was für eine Beziehung zwischen der vertikalen Auslenkung und der Kraft spricht, die durch eine Funktion höherer Ordnung repräsentiert zu sein scheint. Im Allgemeinen war der Elastizitätsmodul der verblendeten Prüfkörper jedoch unabhängig von der Art der Verblendung und wurde daher im Wesentlichen auf die Eigenschaften des Gerüstmaterials PEEK zurückgeführt.

Der Grund für die erhöhte Stabilität der digitalen Verblendung könnte unter anderem die Reduzierung auf wenige komplexe manuelle Schritte im Herstellungsprozess sein.

Im Prinzip ist der einzige manuelle Schritt in diesem Fall die Herstellung des adhäsiven Verbunds zwischen Gerüst und Verblendung, während bei allen anderen Methoden eine Vielzahl von Fehlerquellen im manuellen Herstellungsprozess nicht ausgeschlossen werden kann.

Die Fehler bei diesen Schritten addieren sich auf und beeinflussen im Endeffekt die Stabilität negativ. Ein zweiter Grund könnte das generell höhere Polymerisationsrate der unter optimalen, reproduzierbaren Industriebedingungen hergestellten Präpolymerisate der digitalen Verblendung gegenüber der herkömmlichen manuellen Kompositverblendung sein, da dies mit höheren Festigkeiten assoziiert ist [25].

Der Elastizitätsmodul der geprüften Verblendmaterialien im Vergleich zum Gerüstmaterial PEEK könnte auch einen Einfluss auf die Bruchlast haben. Das in dieser Untersuchung als Gerüstmaterial verwendete PEEK hat einen Elastizitätsmodul von 4,0 GPa während der Elastizitätsmodul des digitalen Verblendmaterials HIPC ebenso wie das visio.lign Verblendmaterial 2,8 GPa betrug, was der niedrigste Wert von allen untersuchten Materialien war. Für die Verblendmaterialien crea.lign und crea.lign Paste, waren die Werte 4,4 respektive 5,5 GPa.

Bei den Prüfkörpern mit den vorgefertigten visio.lign Verblendschalen war der Versagensort nicht im Bereich der Verblendung sondern wie bei den anderen untersuchten Prüfkörpern im Bereich des Verbinders lokalisiert. Dies könnte die gegenüber der digitalen HIPC-Verblendung niedrigeren Bruchlastwerte erklären, da der Bereich, in dem die mit Verblendschalen verblendeten Prüfkörper versagten mit combo.lign verblendet war. Dieser Kunststoff hat einen E-Modul von 8,5 GPa, was in folgenden Untersuchungen Berücksichtigung finden muss. Gleichzeitig sollten Reparaturen an ebensolchen Verblendungen im Bereich der



Verblendschalen mit combo.lign durchgeführt werden, jedoch sollte das Material in allen anderen Bereichen durch ein Elastischeres ersetzt werden.

### **3.2 Verbund zwischen Verblendkunststoff und PEEK: Der Einfluss des Adhäsivsystems und der Korundstrahlparameter**

Die Untersuchung der Verbundeigenschaften zwischen Gerüst- und Verblendmaterialien bei unterschiedlichen Vorbehandlungen und Vorbehandlungsbedingungen im zahntechnischen Bereich rückt mehr und mehr in den Fokus, insbesondere wenn es um neue Materialien wie PEEK geht. Frühere Studien zeigten, dass eine Vergrößerung der Oberfläche durch Strahlverfahren oder ähnliche Prozesse und die Verwendung von MMA-haltigen Adhäsivsystemen zu einer Verbesserung der Verbundeigenschaften zwischen PEEK und Verblendkunststoffen führt [14, 15, 16, 21, 24]. Nach ausgiebiger Recherche gibt es meines Wissens nach derzeitigem Stand noch keine Untersuchungen zum Einfluss der Strahlparameter (Partikelkorngröße und Strahldruck) auf die Verbundeigenschaften zwischen PEEK und gängigen Verblendmaterialien, was deshalb in Kombination mit der Variation des eingesetzten Adhäsivsystems Gegenstand der vorliegenden Studie war.

Im Allgemeinen macht die Verwendung von PEEK in der Zahnmedizin als Gerüstmaterial für dauerhaften festsitzenden Zahnersatz einen stabilen und dauerhaften Verbund mit dem eingesetzten Verblendmaterial erforderlich. Basierend auf den erzielten Ergebnissen mussten die vorher getroffenen Hypothesen dieser Studie gänzlich abgelehnt werden. Zusammenfassend zeigte die vorliegende Untersuchung, dass das Adhäsivsystem ebenso wie einzelne Strahlparameter einen signifikanten Einfluss auf die Verbundeigenschaften zwischen PEEK und dem Verblendsystem hat. Die Parameter der Strahlvorbehandlung beeinflussten die Verbundfestigkeit des adhäsiven Verbunds, wobei der Strahldruck im Gegensatz zur Korngröße einen signifikanten Einfluss zeigte. Die Adhäsivsysteme Scotchbond Universal und Dialog

bonding fluid erreichten sehr hohe Haftungswerte bei erhöhten Strahldrücken, während bei geringerem Druck niedrigere Messwerte beobachtet wurden. Bei hohen Strahldrücken waren die Ergebnisse dieser Systeme bei den Verbundfestigkeitsmessungen vergleichbar mit denen des etablierten Adhäsivsystems visio.link, das in der vorliegenden Untersuchung als positive Kontrollgruppe fungierte da alle vorangegangenen Studien diesem Material sehr hohe Haftwerte bei unterschiedlich vorbehandelten PEEK-Oberflächen attestierten [14, 15, 16, 24]. Auch zeigten diese mit visio.link konditionierten Gruppen die, bei Betrachtung der Überlebensraten, besten Ergebnisse. Auswertungstechnisch wurden für den nichtparametrischen Ansatz die Kaplan-Meier-Schätzungen der kumulativen Ausfallverteilungsfunktion und die robusten Schätzungen für Medianversagensschätzungen ausgewertet. Diese nichtparametrische Analyse bezieht nicht nur die Verletzung der Normalität ein, sondern integriert auch die zweite Schwierigkeit in den erlangten Daten, die Vorversagensfälle.

Die Einbeziehung von Vorversagen in die parametrische Analyse kann die Werte für die tatsächliche Verbundfestigkeit unterschätzen. Die Kaplan-Meier-Analyse behandelt die Werte für vorversagte Exemplare korrekt als zensiert und verwendet die tatsächlichen Messwerte als nicht zensierte Beobachtungen. Die Schätzung der kumulativen Fehlerverteilungsfunktion erfolgt in der Statistik unter dem allgemeinen Begriff der Überlebensanalyse. Häufig wird für konkrete Anwendungen die Überlebensdauer geschätzt. Weniger bekannt ist, dass die nichtparametrische Kaplan-Meier-Methodik für die Analyse anderer primärer Ergebnisse, die einer „Zensur“ unterliegen, sehr nützlich ist, wo die Überlebenszeit beispielsweise durch die Verbund- oder Zugfestigkeit, also der Zugkraft die notwendig ist um einen Prüfkörper zu zerstören, ersetzt wird.

Die Betrachtung der Zusammensetzung von visio.link und dialog bonding fluid könnte darauf hindeuten, dass die Komponente Pentaerythritol Triacrylat (PETIA) eine hohe Potenz zur

Modifizierung der PEEK-Oberfläche aufweist, auch weil visio.link noch höhere Zugfestigkeitswerte lieferte. Die niedrigen TBS-Werte des Monobond Plus / Heliobond-Systems über alle Vorbehandlungen in dieser Studie könnten dem getesteten PEEK-Material zugeschrieben werden, das ungefüllt war, womit keine Elemente an der Oberfläche verfügbar waren, an denen Monobond Plus chemisch binden konnte.

Da die Konditionierung mit Scotchbond Universal (Einflaschensystem) zu höheren Zugfestigkeitswerten führte, muss davon ausgegangen werden, dass das Zwei-Flaschen-System unter bestimmten Bedingungen fehleranfälliger sein kann. Es ist auch denkbar, dass der unmittelbare Kontakt der PEEK-Oberfläche mit dem Dimethacrylat die Bindungseigenschaften verbessert. Durch die Verwendung des Monobond Plus / Heliobond-Adhäsivsystems wird die PEEK-Oberfläche zunächst silanisiert. Darüber hinaus ist es auch denkbar, dass Scotchbond Universal andere Substanzen enthält, die einerseits nicht vom Hersteller benannt werden und andererseits noch nicht bekannt ist, dass sie den Verbund zu partikelgestrahlten PEEK-Oberflächen verbessern.

Während der Experimente dieser Studie wurde festgestellt, dass die PEEK-Oberflächeneigenschaften sich innerhalb von wenigen Minuten nach Durchführung der Vorbehandlung durch Partikelstrahlen erheblich verändern. Eine längere Wartezeit nach der Vorbehandlung führte zu niedrigeren Zugfestigkeitswerten als bei Proben, die unmittelbar nach der Vorbehandlung verblendet wurden. Eine mögliche Erklärung für diese Beobachtung könnte die Oberflächenfeuchtigkeit sein. Luftabrieb, insbesondere bei Hochdruckwerten, führt zu hohen Temperaturen auf der PEEK-Oberfläche und zusätzlich ist die Oberfläche einem sehr trockenen Luftstrom ausgesetzt. Nach einiger Zeit wird die Oberfläche wieder die initiale Feuchtigkeit der Umgebungsluft annehmen. Da die Methacrylate in den Adhäsivsystemen hydrophob sind, könnte dies die Haftfestigkeit stark beeinflussen. Deshalb wurde die Studie gestoppt und alle Exemplare wurden gestrahlt, konditioniert und umgehend verblendet. Unter Bezugnahme auf die Ergebnisse ist die erste Schlussfolgerung, die gezogen werden kann, dass

ein unmittelbarer und kontinuierlicher Workflow - in Bezug auf die Vor- und Nachbearbeitung, Konditionierung und Verblendung - ein wichtiger Aspekt ist, der in Betracht gezogen werden sollte, um gute Bindungseigenschaften an gestrahlten PEEK-Oberflächen zu erreichen. Darüber hinaus kann diese Empfehlung dahingehend erweitert werden, dass PEEK-Gerüste mit hohen Drücken partikelgestrahlt werden sollten.

In dieser Studie führte der verwendete Makro-Zug-Test nach den Messungen ausschließlich zu adhäsivem Versagen bei den Prüfkörpern was als Schlussfolgerung nach sich zieht, dass nur die Verbundzugfestigkeit untersucht und gemessen wurde und die mechanischen Eigenschaften im Verblendkunststoffs nicht in den Messwerten enthalten sind und somit auch keine Aussagen darüber getroffen werden können. Im Gegensatz dazu zeigen Scherversuche oft Kohäsivversagen als Fehlertyp und es ist daher anzunehmen, dass bei diesen Verfahren nicht nur die Adhäsivverbundzugfestigkeit, sondern auch die Gesamtstabilität gemessen wird. Hinsichtlich der Ausgestaltung dieser Studie ist darauf hinzuweisen, dass die Herstellung der Proben auf dem klinischen Prozess beruht, um die Übertragbarkeit der Ergebnisse auf den klinischen Bereich zu ermöglichen, was in vorangegangenen Studien nicht berücksichtigt wurde. Aufgrund der manuellen Vorbehandlung und Verblendung des Gerüstmaterials PEEK zeigten die Prüfkörper bei den Messungen eine realistische statistische Streuung.

Durch manuelles Einspannen der Proben im Probenhalter der Zugvorrichtung können bei der Prüfung kleine Abweichungen hinsichtlich der Zugrichtung aufgetreten sein. Diese wurden mit 3° nach oben abgeschätzt, was zu einem vernachlässigbaren maximalen systematischen Fehler von 0,13% geführt haben kann. Um die klinische Situation zu simulieren, wurde ein thermischer Zyklus als Alterungsverfahren angewendet. Thermische Zyklen werden im Allgemeinen verwendet, um die wechselnden Temperaturen in der oralen Umgebung nachzuahmen. Diese thermischen Änderungen können zu einer Verringerung der Haftfestigkeit führen [31]. Im Gegensatz dazu zeigten andere Studien eine Zunahme der Zugfestigkeit nach der Alterung und behaupteten, dass sie das Postpolymerisationsverfahren unterstützt [26]. Aufgrund der nicht

möglichen genauen Quantifizierung der intraoralen Temperaturänderungen stellen 10.000 thermische Zyklen eine formale Referenz für ein Dienstjahr dar [30]. In dieser Studie wurden die Proben thermisch 20.000 Zyklen ausgesetzt was in etwa 2 Jahren klinischem Einsatz entspricht. Zusammenfassend sind die Ergebnisse dieser Studie daher klinisch relevante Ergebnisse.

Korrekte Vorbehandlung und die Auswahl eines geeigneten Adhäsivsystems verbessert deutlich die Haftwerte und Zugfestigkeit des Verbunds zwischen Gerüst und Verblendung und damit auch die Haltbarkeit. Sowohl der Zahnarzt als auch der Techniker müssen sich genau an die jeweilige Verarbeitungsempfehlung halten. Sowohl die Oberflächenbearbeitung im Labor als auch bei der Behandlung spielt eine entscheidende Rolle bei der Eingliederung der fertigen prothetischen Arbeit und bei der Wahl eines geeigneten Adhäsivsystems. Der Gegenstand künftiger Studien sollte einerseits das beobachtete Phänomen der Verbundschwächung im Falle einer nicht sofortigen Konditionierung der Oberfläche mit dem Adhäsiv nach Vorbehandlung der Oberfläche und andererseits der Einfluss unterschiedlicher Vorbehandlungen und Adhäsivsysteme auf den adhäsiven Verbund mit der präparierten Zahnoberfläche in der klinischen Anwendung sein. Zusätzlich sollte eine klinische Studie mit einem kontrollierten standardisierten Studiendesign die klinische Langzeitperformance von PEEK basiertem permanentem Zahnersatz bewerten.

## 4 Zusammenfassung / Conclusion

### Zusammenfassung

Die gezeigten Untersuchungen führen zu dem grundsätzlichen Ergebnis, dass PEEK als Gerüstmaterial für verblendeten, 3-gliedrigen, festsitzenden Zahnersatz als geeignet betrachtet werden kann.

Langzeituntersuchungen, sowohl in vitro als auch in vivo sind notwendig um die Ergebnisse zu bestätigen und die Weiterentwicklung vor allem der CAD/CAM-Verarbeitung voranzutreiben. Neben den Vorteilen der Abrasions- und Verfärbungsbeständigkeit, die sich in der CAD/CAM-Technik aus der industriellen Großmaßstabsfertigung ergeben, ist der größte Vorteil für die zukünftige klinische Anwendung gegenüber der manuellen Verblendung der niedrigere bzw. beim PAEK-Werkstoffen kein Monomergehalt. Speziell im Kontext der Idee, Legierungen mit hoher allergischer Potenz durch PEEK zu ersetzen ist dies hervorzuheben und sollte Gegenstand zukünftiger Studien sein.

Im Rahmen der Einschränkungen der beiden durchgeführten Studien lässt sich aus den Ergebnissen zusätzlich ableiten, dass der Auswahl des Adhäsivsystems bei der Verblendung von PEEK basierten Gerüsten hohes Augenmerk gelten muss. Dies gilt im Speziellen für die chemische Zusammensetzung, da gezeigt werden konnte, dass bestimmte Inhaltsstoffe eine hohe Potenz haben den Verbund zu verbessern.

Von den getesteten Adhäsivsystemen zeigte visio.link die besten Hafteigenschaften und die kleinste Anzahl von Prüfkörpern, die schon bei der Alterung versagten. Scotchbond Universal und Dialog bonding fluid konnten unter Voraussetzung der Strahlvorbehandlung mit 0,35 MPa ähnlich hohe Zugfestigkeitswerte wie visio.link erreichen was aber ausschließlich auf die genannten Bedingungen zutreffend ist. Das kombinierte Adhäsivsystem aus Monobond Plus und Heliobond zeigte die meisten Fälle von Prüfkörperversagen bei der Alterung und auch die niedrigsten Zugfestigkeiten aller untersuchten Systeme. Der Strahlruck zeigte im Gegensatz zur Strahlpartikelgröße einen signifikanten Einfluss auf die Verbundfestigkeit. Die besten

Ergebnisse wurden beim höchsten untersuchten Strahldruck von 0,35 MPa erzielt. Es ist nicht auszuschließen, dass höhere Strahldrücke noch bessere Ergebnisse liefern, weshalb Gegenstand folgender Untersuchungen eine größere Bandbreite mit gleichzeitig mehr Zwischenwerten von Strahlparametern im Bereich oberhalb von 0,35 MPa sein sollte.

## **Conclusion**

Facing the studies one conclusion is that PEEK can be considered as a suitable framework for FDPs. Long-term studies, both in vitro and in vivo, are necessary to confirm the results and to promote further development, especially of CAD / CAM processing. In addition to the advantages such as wear resistance, very homogeneous polymerization and a lower discoloration potential resulting from large-scale industrial production in CAD / CAM technology, the greatest advantage for future clinical application compared to manual veneering is the lower monomer content. Within the limits of the two studies, it can also be derived from the results that the selection of the adhesive system is very important for durable veneering of PEEK-frameworks. This applies in particular to the chemical composition

since certain ingredients have a high potency to improve the bonding to PEEK surfaces. Among the tested adhesive systems, visio.link showed the best properties and the smallest number of test specimens that already failed during aging. Scotchbond Universal and Dialog bonding fluid were able to achieve similarly high tensile bond strength values as visio.link when using air-abrasion with 0.35 MPa only. The combined adhesive system of Monobond Plus and Heliobond showed the majority of cases of failure of the test specimens during aging and the lowest TBS values of all the systems under investigation. In contrast to the particle size, the beam pressure showed a significant influence on the tensile bond strength. The best results were obtained at the highest beam pressure of 0.35 MPa. It can not be ruled out that higher pressures provide even better results, which is why the subject of the following investigations should be a larger

bandwidth with simultaneous more intermediate values of airborne particle abrasion pressure values in the range above 0.35 MPa.



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